An examination of chemistry and transport processes in the tropical lower stratosphere using observations of long-lived and short-lived compounds obtained during STRAT and POLARIS.

F. Flocke,[1] R.L. Herman,[2] R.J. Salawitch,[2] E. Atlas,[1] C.R. Webster,[2] S.M. Schauffler,[1] R.A. Lueb,[1] R.D. May,[2] E.J. Moyer,[3] K.H. Rosenlof,[4] D.C. Scott,[2] D.R. Blake,[5] and T.P. Bui[6]

[1]NCAR/ACD, P.O. Box 3000, Boulder, CO 80307-3000

[2]NASA/JPL, 4800 Oak Grove Dr., Pasadena, CA 91109

[3]Division of Geological and Planetary Sciences, California Institute of Technology, Mail Stop 150-21, Pasadena, CA 91125

[4]NOAA/AL, 325 Broadway, Boulder, CO 80303

[5]University of California at Irvine, Dept. of Chemistry, Irvine, CA 92697

[6]NASA/Ames Research Center, Mail Stop 245-5, Moffett Field, CA 94035-1000

Abstract

A suite of compounds with a wide range of photochemical lifetimes (3 months to several decades) was measured in the tropical and mid-latitude upper troposphere and lower stratosphere during the Stratospheric Tracers of Atmospheric Transport (STRAT) experiment (fall 1995, winter, summer and fall 1996) and the third Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) deployment in late summer 1997. These species include various chlorofluorocarbons, hydrocarbons, halocarbons, and halons measured in whole air samples, and CO measured *in situ* by tunable diode laser spectroscopy. Mixing ratio profiles of long-lived species in the tropical lower stratosphere are examined using a one-dimensional photochemical model that includes entrainment from the extra-tropical stratosphere and is constrained by measured concentrations of OH. Profiles of tracers found using the 1-D model agree well with all the observed tropical profiles for an entrainment time scale of 8.5^{+5}_{-3} months, independent of altitude between potential temperatures of 370 and 500 K. The tropical profile of CO is used to show that the annually averaged ascent rate profile, based on a set of radiative heating calculations, is accurate to $\pm20\%$, a smaller uncertainty than found by considering the uncertainties in the radiative model and its inputs. Tropical profiles of CO and ethane reveal that the concentration of Cl is higher than expected based on photochemical model simulations using standard gas phase kinetics and established relationships between total inorganic chlorine and CFC-11. Our observations suggest that short-lived organic chlorinated compounds and HCl carried across the tropical tropopause may provide an important source of inorganic chlorine to the tropical lower stratosphere that has been largely unappreciated in previous model studies. The entrainment time scale found in our study is considerably less than the value found by a similar study that focused on observations obtained in the lower stratosphere during 1994. Several possible explanations for this difference are discussed.

1. Introduction

Dynamical processes in the tropical lower **stratosphere** can have an important impact on the physical and chemical processes that, for example, influence radiative forcing, **heating budgets**, and **ozone photochemistry** (see *Holton et al.*, [1995] and references therein). Tracer observations obtained in the tropical stratosphere suggest a strong degree of isolation of the region of large scale tropical ascent (roughly within 15° of the equator) from the mid-latitude stratosphere [e.g., *Boering et al.*, 1994; *Boering et al.*, 1996; *Mote et al.*, 1996; *Murphy et al.*, 1993; *Randel et al.*, 1993; *Trepte and Hitchman*, 1992; *Wofsy et al.*, 1994]. To address these observations, *Plumb* [1996] developed the "tropical pipe" model of stratospheric circulation that essentially isolates air in the tropical upwelling region from air at mid-latitudes. However, it has been shown that a limited amount of irreversible mixing must occur between mid-latitude- and tropical air in the lower stratosphere to accurately describe the tracer observations obtained in the tropics [e.g., *Avallone and Prather*, 1996; *Hall and Waugh*, 1997; *Herman et al.*, 1998a; *Minschwaner et al.*, 1996; *Mote et al.*, 1998; *Schoeberl et al.*, 1997; *Volk et al.*, 1996]. Because this mixing process plays an important role for the redistribution of pollutants released at mid latitudes to higher altitudes, in particular with respect to a proposed fleet of supersonic aircraft [*Stolarski*, 1995], emphasis has been placed recently on quantifying the characteristic "entrainment time scale" for irreversible mixing of mid-latitude stratospheric air into the tropical stratosphere. Previous studies have suggested that **entrainment** is fastest below 20 km [e.g., *Herman et al.*, 1998a; *Minschwaner et al.*, 1996; *Mote et al.*, 1998; *Schoeberl et al.*, 1997], but this conclusion has been limited by large uncertainties related to the calculated ascent rate in the tropics as well as the use of tracers with photochemical lifetimes sufficiently long that key assumptions could not be tested. This study uses a unique set of tracer observations obtained aircraft measurement during the STRAT and POLARIS missions on board the NASA ER-2 aircraft [see *Fahey et al.*, this issue] by the Whole Air Sampler (WAS) and the Aircraft Laser Infrared Absorption Spectrometer (ALIAS). The suite of tracers analyzed here covers a range of local photochemical

lifetimes between 3 months and several hundred years.

We use a 1-D photochemical transport model to simulate the altitude profiles of the volume mixing ratios (referred to as "vmr profile" below) of tracers observed at altitudes between 16 and 20.5 km in the tropics [*Herman et al.*, 1998a]. Since the abundances of many of the species are strongly influenced by various chemical loss processes, the photochemistry applied in the model needs to be realistic. We use both a photochemical steady-state model of the lower stratosphere and *in situ* observations of radicals made on board the ER-2 to estimate photochemical removal rates. The measurements of the vmr profiles of the short-lived species are used to optimize the radical concentrations (in particular the chlorine radical chemistry) used in the model as well as to constrain the ascent rate profile used in the model. The vmr profiles of the long- and medium- lived species are then used together with the optimized ascent rate and chemistry to constrain the average entrainment time scale. Finally, we compare our results to earlier studies and discuss possible implications.

2. Experimental

Whole air sampler (WAS). The main component of WAS is a set of 29 to 49 specially treated stainless steel canisters that are filled with ambient air to a pressure of about 3000 hPa in flight by means of an all-metal bellows pump [*Heidt et al.*, 1989]. The filling time varies with flight altitude between less than 10 sec in the upper troposphere to about 200 sec at 21 km. During three of the tropical flights we programmed the WAS to acquire samples with the highest possible frequency to achieve good altitude coverage, i.e. about 20-25 samples per dive. The canisters are transported back to NCAR and analyzed in the laboratory. About 50 different species including CFC, HCFC and HFC, halons, other halogenated compounds and alkyl nitrates are quantified by gas chromatography - mass spectrometry (GC-MS, HP 5890/5971), operated in single-ion-mode. The mixing ratios of methane (CH_4) and light hydrocarbons (C_2 to C_4) are measured using gas chromatography – flame ionization detection (GC-FID, HP 5890). The limit

of detection (LOD) for the non-methane hydrocarbons is about 2 parts per trillion by volume (pptv) and the precision of the measurement is better than 2% or 2 pptv. In the case of the GC-MS instrument, LODs for the different species vary because of different specific responses and background noise for the quantitation ions used, but are generally better than 0.1 pptv. The measurement accuracy also varies because of different individual relative responses, but an overall estimate of better than 5% or the LOD (whichever is larger) can be made. More details about our analytical procedures, canister preparation, etc. can be found in [*Daniel et al.*, 1996; *Flocke et al.*, 1998; *Schauffler et al.*, 1998a]. We note that, specifically for the short-lived species, the accuracy of our measurements can be limited by variable background concentrations of these substances in the canisters (caused by outgassing of the sampling lines, the manifold system, or the canister walls) rather than by the LOD of the analytical instrument. We will discuss these background issues and their effect on the model analyses later in the manuscript.

Aircraft Laser Infrared Absorption Spectrometer (ALIAS): ALIAS is a high-resolution, mid-infrared absorption spectrometer using four tunable diode lasers (TDLs) to simultaneously measure the concentration of CO, N_2O, CH_4, and HCl. Ambient air is drawn into a Herriott cell with a light path of 80 m and a flush time of less than two seconds. The system has been described in detail in *May and Webster* [1993] and *Webster et al.* [1994]. For CO, the instrument precision (±1 standard deviation) is ±0.7 parts per billion by volume (ppbv) for a 3-second average value. The estimated instrument accuracy (±1 standard deviation) is ±5% relative to the calibration standards supplied by the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL).

Harvard HO_x instrument: The concentration of the hydroxyl radical (OH) is a critical parameter for our model calculations. *In situ* measurements of OH and HO_2 were made on board the ER-2 by the Harvard HO_x instrument. The instrument is based on UV laser-induced fluorescence and is described by *Wennberg et al.* [1994a]. The accuracy and precision of the OH

measurement are stated to be ±25% and ±0.10 pptv, respectively. The measured OH concentration is a strong function of solar zenith angle [e.g., *Salawitch et al.*, 1994; *Wennberg et al.*, 1994b], but is relatively independent of altitude in the tropical lower stratosphere [*Herman et al.*, 1998b]. *Herman et al.* used a quadratic fit of the observed OH concentration as a function of solar zenith angle to obtain an annual, 24-hour mean OH concentration of $8\pm3\times10^5$ cm^{-3} for the tropical lower stratosphere. All subsequent chemical calculations are performed using this concentration.

Meteorological parameters (MMS): Temperature and pressure were obtained from *in situ* measurements made by the ER-2 Meteorological Measurement System (MMS), which is described in detail by *Scott et al.*, [1990].

Flights: Data were analyzed for six equatorial survey flights of the ER-2, going south from Barbers Point Naval Air Station, Oahu (21°N, 158°W) to about 3°S latitude along (±5°) the 160°W meridian. Measurements of the NO_y/O_3 ratio [*Murphy et al.*, 1993] confirm that tropical air was sampled during periods of each of these flights (see below). Five of these flights were performed during the STRAT program on 5 Nov. 1995 (referred to as 951105) and on 13 Feb., 1 Aug., 8 Aug., and 11 Dec. 1996 (960213, 960801, 960808, 961211, respectively). One flight was performed during POLARIS on 23 Sept. 1997 (970923). All instruments reported data for each flight except that the WAS did not fly on 951105. Tracer concentration profiles at mid-latitudes were obtained from stair-step flights and ascents/descents of the ER-2 out of NASA Ames Research Center (37.4°N, 122.0°W) made during numerous STRAT and POLARIS flights from all seven deployments of the ER-2 between Nov. 1995 and Sept. 1997. In addition, we used results from canister analyses of samples collected by the WAS in the upper troposphere during the PEM-Tropics mission [*Atlas et al.*, 1998; *Hoell*, 1998; *Schauffler et al.*, 1998b] on board the NASA DC-8 and P3B aircraft in late summer 1996 to infer the interhemispheric gradients of the tracers mixing ratios (see below).

3. Model

Approach. We simulate vertical profiles of measured tracers in the tropical lower stratosphere using a one-dimensional model that includes vertical advection, horizontal entrainment of extra-tropical air, and full photochemistry for each species. The model assumes that the tropical mixing ratio χ of each tracer is controlled by local photochemical production and loss as well as by mixing with air parcels entrained from the extra-tropics. This approach is similar to that made by *Volk et al.* [1996]. The mixing ratio χ of a species with a local lifetime to photochemical loss τ_{chem} and a production term P is described by:

$$Q \cdot \frac{\partial \chi}{\partial \theta} = P - \frac{\chi}{\tau_{chem}} - \left[\frac{\chi - \chi_{ML}}{\tau_e} \right] - \gamma \chi, \tag{1}$$

where θ is the potential temperature, Q is the tropical net diabatic heating rate, χ_{ML} is the mixing ratio of the species at mid latitudes (at the same θ-level as χ), τ_e is the mean characteristic time for the entrainment of extra-tropical air, and $\gamma\chi$ is a term to account for the mean tropospheric growth rate of the species (averaged over the 1994-1997 time period for our data):

$$\gamma = \frac{\partial \chi_{trop}}{\partial t} \cdot (\chi_{trop})^{-1}, \tag{2}$$

where χ_{trop} is the mean tropospheric mixing ratio. We assume that mixing occurs only along isentropic surfaces, that the tropical air sampled is representative of the large-scale ascent region (i.e., horizontal homogeneity in the tropics for the time of the observation) and that the extra-tropical air is described by an average altitude profile for each species (based on observations) which are representative of mid-latitudes and unaffected by the mixing process. Equation (1) is solved for $\chi(\theta)$ to calculate profiles of the tropical mixing ratio of each species for various assumptions regarding τ_e, τ_{chem}, Q, P (considered only for CO), and χ_{ML}. The entrainment time scale, τ_e, is determined based on the similarity of modeled and measured profiles in the tropics for the suite of tracers. We show in the discussion section that uncertainties in the mid-latitude tracer profiles, χ_{ML}, have the largest effect of any input model parameter on the derived value of τ_e.

Unlike the approach of *Volk et al.* [1996], we use our model to simulate the observed vmr profiles rather than using tracer-tracer correlations to infer τ_e. Our approach does not eliminate the need to use calculated mean heating rates to estimate τ_e, but does provide the opportunity to establish whether a unique set of ascent rates, entrainment time scales and chemical conditions can be found that fit all the observed vmr profiles of a large number of tracers. The unique contribution of this paper is the use of short-lived species CO, ethane and C_2Cl_4 to constrain ascent rates and Cl concentrations, which improves the accuracy of the entrainment time scales estimated from the observed distributions of the long-lived species.

Photochemical steady-state model. The photochemical loss terms required for equation (1) involving photolysis and reactions with O^1D or Cl were generated using the photochemical steady state (PSS) model described by *Salawitch et al.* [1994]. All reaction rates and photolysis cross sections necessary are from *DeMore et al.* [1997], unless noted otherwise. Photolysis rates and quantum yields for CH_3Cl, CFC-11, CFC-12, CFC-113, CFC-114, H-1211, H-2402, C_2Cl_4 and CH_3Br are obtained from a recent review by *Roeth et al.* [1998]. A recently measured rate coefficient for the reaction of tetrachloroethene (C_2Cl_4) with OH [*R. Talukdar*, private communication, 1998] is used.

Twenty-four hour mean photolysis rates for the measured tracers are generated from actinic flux calculations at each potential temperature level of the 1-D model (see below) and for variations in solar zenith angle corresponding to 15 minute increments throughout the day (e.g., 97 PSS model time intervals per day). The PSS model is constrained by the mean tropical profiles of O_3 and temperature obtained by the ER-2 and OMS balloon platforms [*Herman et al.*, 1998a] between 0 and 30 km and by a climatology based on satellite observations [*Minschwaner et al.*, 1993; *Salawitch et al.*, 1994] for altitudes between 30 and 80 km. The total column abundance of O_3 corresponding to model profiles of O_3 derived in this manner for specific times and locations of tropical flights of the OMS package typically agrees with total O_3 measurements obtained by

the TOMS satellite to within 5 DU. Model input profiles of CH_4, H_2O, CO, ethane, NO_y, total

inorganic chlorine (Cl_y) and aerosol surface area (necessary to calculate concentrations of OH, the

atomic chlorine (Cl) mixing ratio, and O^1D) are derived from ER-2 observations in the tropics.

The 24-hour mean concentration of OH based on *in situ* observations is used in the 1-D

model described below due to discrepancies between theory and observation of OH that are not

completely resolved. The calculated OH tends to agree with observation to better than 15% near

20 km, with greater discrepancy (the modeled OH is less than measured OH, by as much as a

factor of two) at lower altitudes. This discrepancy is consistent with the tendency of the model,

using measured NO_y, to underestimate observed NO (see *Osterman et al.* [1998] and *Gao et al.*

[1998] for a discussion of a possible resolution to the discrepancy for stratospheric NO/NO_y).

Constraining the model using measured NO improves the agreement with measured OH in the

tropical lower stratosphere, but this calculation still tends to underestimate measured OH,

particularly in the lowermost stratosphere. This discrepancy may indicate the influence of

hydrogen radical precursors such as acetone or peroxides [*Jeagle et al.*, 1997; *Singh et al.*, 1995;

Wennberg et al., 1998] that are unaccounted for in the model, owing to a lack of a measurement

of this species in the tropical lower stratosphere. The observed concentration of OH in the tropics

during the ER-2 flights described above exhibits a marked variation with solar zenith angle, but

little dependence on altitude [*Herman et al.*, 1998b]. Consequently, for the 1-D model

calculations described below, we use a value for the 24-hour mean concentration for OH of

$8\pm3\times10^5$ cm^{-3}, independent of altitude, that was derived by *Herman et al.* [1998b].

Carbon monoxide (CO) is the only tracer under consideration for which photochemical

production is important. Production of CO from reactions of CH_4 with OH, O^1D, and Cl is

calculated using measured profiles of CH_4, 24-hour mean concentration profiles of O^1D and Cl

resulting from full diurnal PSS simulations at each potential temperature level, and the empirical

24-hour mean concentration of OH described above. Production of CO tends to be dominated by

reaction of CH_4 with OH below about 480 K, with the reaction of CH_4 with Cl becoming

important above this θ level.

The mixing ratio profile of Cl_y is an important and somewhat uncertain model input parameter. Reaction with Cl is an important loss process for a number of molecules considered here (see Table 1), and the calculated concentration of Cl is to first order linearly dependent on Cl_y. Typically, vmr profiles for Cl_y used in photochemical models are generated from empirical relations between tropical measurements of the total chlorine content of the organic source molecules (CCl_y) and a tracer such as CFC-11, combined with the mean tropical vmr profile for CFC-11. As will be discussed below, Cl_y estimated in this manner for the tropical lower stratosphere is particularly uncertain due to the possible contribution of inorganic chlorine from the decomposition (in both the troposphere and stratosphere) of very short-lived organic compounds that are not typically considered in the definition of CCl_y. Various assumptions regarding model constraints for the vmr profile of Cl_y are considered, as described below.

We note that *in situ* observations of ClO obtained in the tropics for potential temperatures below 460 K on 970923 provide little constraint on calculated Cl. The measured vmr of ClO was below 15 pptv (near the detection limit) and displayed considerable scatter, with numerous individual 30 sec average determinations lying below zero [*R. Stimpfle* et al., private communication, 1998]. The large uncertainty in measured ClO cannot be used to rule out any of the various Cl profiles considered below. Finally, the *in situ* ClO instrument was not flown on any of the tropical ER-2 flights during the STRAT campaign. The observations of HCl, which provide a strong test of the model representation of inorganic chlorine partitioning when Cl_y is known accurately (e.g., at higher altitudes [*Sen et al.*, 1998]), are used here to better constrain our knowledge of Cl_y. This seems appropriate since HCl ≈ Cl_y for the conditions (e.g., temperature, humidity, and aerosol surface area) of the tropical lower stratosphere using rates for heterogeneous reactions involving HCl given by *DeMore et al.* [1997].

Table 1 lists for each compound the main loss process and the local photochemical

lifetime at different potential temperature levels. These values were obtained from an "annual" average of PSS model runs for solar conditions appropriate for equinox and the two solstices, keeping O_3 and tracer profiles fixed at their mean tropical values. The interhemispheric gradients and boundary conditions required for the 1-D model simulations (see below) are also given in Table 1.

One-dimensional model. As noted above, we simulate the vertical profiles of gases in the tropical lower stratosphere with a 1-D photochemical model described by equation (1). The diabatic heating rate Q is calculated using a model of infrared radiative transfer that is mass-balanced (e.g., constrained by zero net mass flux through a global pressure surface [*Rosenlof*, 1995]). The O_3 vmr profiles used in the radiative transfer model are inferred from UARS satellite observations. To obtain a representative profile of mean tropical heating rates, Q is averaged over deep tropical latitudes (9.5°S to 9.5°N), all longitudes, and both phases of the quasi-biennial oscillation (QBO) during the time of the ER-2 flights (July 1995 through June 1997). The 1-D model has fourteen discrete levels equally spaced in log(pressure). The boundary condition for the mixing ratio of each species at the mean isentrope of the tropical tropopause, $\theta = 370$ K, is derived from the tropical ER-2 flights. Equation (1) is numerically solved for $\chi(\theta)$ with Mathematica® (Wolfram Research, Champaign, IL), which uses cubic splines to interpolate between levels. The value of τ_e is varied (see below) and agreement with the measured tracer profiles is tested.

We have simulated the observed vmr profiles of a suite of twelve short- and long-lived tracers: CO, ethane, C_2Cl_4, CH_3Br, the halons H-1211 and H-2402, CH_3Cl, CFC-11, CFC-12, CFC-113, CFC-114, and CH_4. The tropical data were selected using the NO_y/O_3 ratio gradient measured on the ER-2 [*Fahey et al.*, 1985; *Proffitt and McLaughlin*, 1983], which is strongly negative towards the tropics and therefore can be used to identify tropical air [*Murphy et al.*, 1993]. Typically, this resulted in the selection of data equatorward of 10° to 6°N. The average

extra-tropical mixing ratio profile for each species was synthesized in two steps. First, data taken by WAS and ALIAS between 30 and 55°N during STRAT and POLARIS were averaged into mean vmr profiles. We assumed that below the 420 K potential temperature surface, extra-tropical stratospheric profiles in each hemisphere are influenced by mixing with the upper troposphere. Above 420 K, the upper troposphere should have negligible influence on the composition of stratospheric air parcels [e.g., *Holton et al.*, 1995]). Hence, we assume that the annual mean tracer distribution above 420 K is identical for both hemispheres. This assumption is supported by satellite and aircraft observations of, for example, N_2O and CH_4 [*Michelsen et al.*, 1998; *Randel et al.*, 1993; *Randel et al.*, 1998; *Tuck et al.*, 1997a]. Extra-tropical stratospheric profiles below 420K were obtained by scaling the mean profiles measured in the northern hemisphere by half of the observed interhemispheric gradient of the mixing ratio of each species. The interhemispheric gradients (see table 1) were calculated from data taken by the DC-8 WAS system [e.g., *Blake et al.*, 1996a] during the PEM-Tropics mission in early fall 1996 [*Hoell et al.*, 1998]. Only upper tropospheric measurements (i.e. from flight altitudes above 9 km) between 30°N and 55°N and between 30°S and 55°S were used. The vmr profiles derived in this manner were used to represent in the model the average composition of mid-latitude air mixed into the tropics. The profiles are also plotted in Figure 4 for comparison with the tropical data.

Boundary conditions for the model were established using data obtained from the ER-2 during the tropical dives below 17.5 km altitude by the DC-8 during PEM-Tropics at altitudes above 10 km within 5° of the equator. Tracer concentrations at the tropical tropopause were estimated from these observations (see table 1) and used to initialize the model at the $\theta = 370$ K level.

The 1-D model neglects vertical diffusion. *Mote et al.* [1998] and *Hall and Waugh* [1997] have shown that vertical diffusion has a small effect on the abundance of tropical tracers compared to the effect of vertical advection. Photochemical production and loss rates were

computed for each species and potential temperature level using 24 hour average photolysis rates and concentrations of O^1D resulting from a full diurnal run of the PSS model. Finally, the growth rate term in equation (1), $\gamma\chi$, was calculated from global mean tropospheric trends during the period 1994 to 1997 [*Dlugokencky et al.*, 1997; *Frazer et al.*, 1998; *Montzka et al.*, 1996; *Travnicek et al.*, 1998; *S. Montzka*, private communication] (see table 1). The growth rate was assumed to be negligible for CFC-114, CH_3Cl, CH_3Br, CO, ethane, and C_2Cl_4.

4. Results

In the following discussion different transport processes and the chemical schemes applied in the model are examined. We note that all model runs shown in figures 2, 3 and 4 were performed using the optimized set of parameters, except for the parameter that was varied, to demonstrate its influence on the model results. The process of finding the correct set of parameters involved many iterations as well as extensive testing of different possible combinations of chemistry and transport that are not described for the purpose of clarity. However, the reader should bear in mind that we are using an independent estimate of the ascent rate based on radiative heating calculations (tested by comparison with tracer vmr profiles), and that the range of calculated concentrations of Cl is narrowed considerably by the *in situ* measurements of the short-lived tracers. The discussion below will demonstrate that the observed vmr profiles of individual tracers and the correlation of CO *vs.* ethane do in fact provide a strong constraint on the mean ascent rate in the tropical upwelling region and on the mean chlorine atom concentration in the lower tropical stratosphere.

Short-lived species and chlorine chemistry. If τ_{chem} is small enough that the chemical loss term in equation (1) dominates the quasi-horizontal mixing term, the altitude profile of a tracer is primarily sensitive to chemistry and nearly independent of the mixing time (τ_e) as well as the assumed vmr profile at mid-latitudes (χ_{ML}). The simulation of measured tropical vmr profiles of CO, ethane and C_2Cl_4, tracers with very short lower stratospheric lifetimes on the order of a few

months, are discussed below and used to optimize constraints for Cl_y applied to the model.

The chlorine atom concentration is a critical parameter for the chemistry of the lower tropical stratosphere. It must be realistic to calculate accurate chemical loss rates. It is calculated in the standard version of the PSS model using total inorganic chlorine (Cl_y) as a direct input parameter, utilizing an empirical relationship between CFC-11 and Cl_y based on ACATS measurements of the major organic source molecules (CCl_y) [*Elkins et al.*, 1996]. Total inorganic chlorine is calculated from ACATS CCl_y using observed SF_6 concentrations to estimate the age of the sampled air mass in order to account for the slight decrease of CCl_y with time for the contemporary troposphere [*J. Elkins*, private communication].

The model probably tends to underestimate the actual Cl concentration in the lower tropical stratosphere when the ACATS relation for Cl_y is used. This Cl_y relation does not account for several short-lived organic chlorine-containing species that are not measured by ACATS, e.g. methylene chloride, chloroform and the bromochlorocarbons. This potential influence of short-lived source gases on lower stratospheric halogen chemistry has been suggested in the literature [*Ko et al.*, 1997; *Schauffler et al.*, 1998b; *Solomon et al.*, 1994]. Many of these short-lived chlorinated species are measured by WAS and can account for more than 100 pptv of organic chlorine in the tropical upper troposphere. Also, several of the HCFC molecules with rapidly rising tropospheric concentrations are not included in the ACATS relationship. Furthermore, there are large uncertainties in the concentration of HCl in the lowermost tropical stratosphere. Calculated mixing ratios of HCl at the tropical tropopause are 5 pptv or less. In contrast, during the POLARIS flight on 970923, the ALIAS data at the tropical tropopause is close to the LOD, but allows to estimate an upper limit for the HCl mixing ratio of 200 pptv.

To investigate the model sensitivity to assumptions regarding Cl_y, we produced an alternative relation for Cl_y using total organic chlorine (CCl_y) as measured by WAS. We calculated the mixing ratios of Cl_y based on the average reduction of the WAS CCl_y at each potential temperature level compared to the average CCl_y at the tropical tropopause. A correction

for the overall trend of the tropospheric total chlorine burden was not made for this calculation, but this is unimportant since the age of air in the lower tropical stratosphere is only on the order of one year [e.g., *Boering et al.*, 1996]. Since the total chlorine burden of the troposphere is decreasing with time, not including a correction will give a conservative estimate with regard to Cl_y. The boundary condition for Cl_y at the tropical tropopause was set to 200 pptv, based on the upper limit for HCl observed by ALIAS. This estimate for Cl_y is based on measurements entirely and does not rely on any assumptions regarding unmeasured species.

Figure 1 shows the chlorine atom concentration versus potential temperature calculated by the PSS model using both the ACATS and WAS/ALIAS assumptions for Cl_y. Also shown is the optimized chlorine concentration profile that provides best agreement with the measured mixing ratio profiles of ethane and CO (see below). We also show a "high Cl" profile in figure 1, which was derived by multiplying the PSS model profile based on WAS/ALIAS Cl_y by a factor of four. This high Cl profile is used below to investigate the sensitivity of calculated profiles of CO, ethane, and C_2Cl_4 to assumptions regarding atomic Cl. The multiplicative factor of four used for this profile was arrived at based on considering the uncertainties in Cl_y, uncertainties in the rate coefficients that describe the Cl/ClO ratio and the reaction of OH + HCl near 200 K, as well as the tendency of the PSS model to underestimate the observed concentration of OH in the lowermost tropical stratosphere by nearly a factor of three (i.e., allowing in the PSS model for a "missing" source of HO_x strong enough to match measured OH will lead to a significant rise in calculated Cl due to the influence of the OH + HCl reaction). This multiplicative factor is unlikely to be realistic for the higher altitudes (e.g., $\theta > 460K$) because theory and observation of OH are in much better agreement and the fractional uncertainty in Cl_y is much smaller. The large differences in the three model profiles for Cl illustrated in figure 1 demonstrate that our ability to constrain the concentration of atomic chlorine using the PSS model is rather limited for the tropical lowermost stratosphere.

We therefore derived an optimized Cl concentration profile by running our 1-D model to

match the observed altitude profiles of the short-lived tracers. Ethane and C_2Cl_4 are particularly sensitive to the concentration of Cl in the lower stratosphere (their reaction rates with Cl are several hundred times faster than the rates for reaction with OH). Below $\approx$ 480K, CO is relatively insensitive to Cl, but production of CO from $CH_4 + Cl$ becomes important at higher altitudes. Because the input concentration of OH was constrained by the measurements, OH was not varied to optimize the Cl concentration. Varying OH within the estimated measurement uncertainty has little effect on the optimized concentration of Cl. We also did not vary the O^1D profile predicted by the model. The impact of uncertainties in O^1D on the chemical loss rates of the species we analyze here is relatively small for the lower stratosphere, because the reaction with O^1D is not the major loss process for any of the species analyzed (see table 1). The photolysis rates calculated by the PSS model were also adapted into the 1-D model unchanged.

The optimized concentration for Cl lies within the range of the PSS model calculations, given the uncertainties in model input parameters described above. While it may be tempting to attribute the difference between the Cl profile found using the WAS/ALIAS constraint for Cl_y and the optimized Cl profile to the influence of heterogeneous processes not represented in the PSS model, we note that the calculated profile for NO agrees with observation to better than 20% between 380 and 420K for the tropical flight of 970923. The tropical observations of NO obtained during STRAT and POLARIS suggest the heterogeneous sink of NO_x is treated in a reasonable fashion by the PSS model, although this conclusion is complicated by the inability of the model to properly simulate observed concentrations of OH [*Herman et al.*, 1998b]. The large uncertainties in the rate coefficient for gas phase processes such as OH + HCl (e.g., Figure 2 of [*Michelsen et al.*, 1996]), ClO + O, and Cl + O_3 for temperatures near 200K as well the uncertainty in the model profile for Cl_y make it unclear whether "missing chemistry" is necessary to explain the optimized profile for Cl derived from the tracer observations.

Figures 2a to 2c show the measured mixing ratios of CO, C_2Cl_4 and ethane versus potential temperature, and figure 2d shows a correlation plot of the measured mixing ratios of

ethane versus CO. Also shown are 1-D model simulations using three profiles of 24 hour mean chlorine atom concentrations: 1) the PSS model Cl profile using the "standard" WAS/ALIAS Cl_y constraint, 2) the optimized Cl profile and 3) the upper limit Cl profile (figure 1). An entrainment time of 8.5 months was used in all cases (the entrainment time does not have a significant influence on the predicted altitude profiles of these species). It can be seen in figure 2a that the upper-limit chlorine profile is unreasonable since it significantly increases the steady-state CO mixing ratio above 460 K, owing to increased production from the reaction of chlorine atoms with CH_4. At potential temperature levels below 440K, the chlorine atom concentration does not significantly change the predicted CO mixing ratio, but has a strong influence on the predicted profiles of ethane and C_2Cl_4, as demonstrated in figures 2b and 2c. Although the optimized Cl profile somewhat underestimates the observed vmr of CO and ethane around 440 K, it fits the observed CO to ethane ratio very well, as shown in figure 2d. During the 960801 flight we encountered unusually "photochemically young" air masses at the 440 K level that were not representative of the region sampled, which can also be seen in several other tracer profiles (see figures 3 and 4). The optimized chlorine profile also fits the observed C_2Cl_4 altitude profile, given that the C_2Cl_4 data are quite scattered. This scatter is probably attributable mainly to the large interhemispheric gradient of C_2Cl_4 in the upper troposphere as well as to background levels in some sample flasks (see below). We note, however, that the kinetic data recommended for the reaction of C_2Cl_4 with OH in *DeMore et al.* [1997] did not allow for a reasonable fit of the C_2Cl_4 altitude profile. A new measurement of this rate constant made by *Talukdar et al.* [*R. Talukdar*, private communication], who report the same room temperature rate coefficient but a significantly smaller temperature dependency for this reaction than given by *DeMore et al.* [1997], leads to a much faster rate coefficient under lower stratospheric conditions. Our model results are based on these new laboratory data.

Both C_2Cl_4 and ethane show measurable mixing ratios above the 460 and 470 K levels, respectively, even though the modeled mixing ratios approach zero. This is likely caused by a

small measurement artifact caused by outgassing of the canister walls, the inlet line and/or the inner surfaces of the pump. These background levels vary between 0 and 20 pptv of ethane and between 0 and 0.1 pptv C_2Cl_4, which makes it very difficult to correct each individual canister but may, on the average, account for the "residual" concentrations measured at high altitudes. Removing an average artifact of 15 pptv for ethane and 0.05 pptv for C_2Cl_4 produces negative concentrations for about 30% of the samples but overall improves the model/measurement comparison at the highest altitudes.

In summary, we believe that the chlorine atom concentration profile inferred from the short-lived tracer measurements provides a better estimate of the actual concentration of Cl than the calculated Cl by the PSS model owing to uncertainties in Cl_y and relevant kinetic processes. Without changing any other chemical loss variables, it provides a very good fit to the observed altitude profiles of different species that have very different sensitivities to the concentration of Cl.

Ascent rates: The stated uncertainty of the ascent rates used in the 1-D model is on the order of ±50%, based on the inherent uncertainties of heating rate calculations [*Rosenlof,* 1995]. This raises the question whether it may be possible to find a different combination of entrainment rates and chemical conditions that would offset a change in the model ascent rate profile and still fit the observed tracer profiles. Figure 3a demonstrates that the observed vmr profile of CFC-12 can be adequately simulated by using 30% reduction of the ascent rates and an entrainment time of 13.5 months [*Volk et al.*, 1996] instead of our optimized entrainment time of 8.5 months (see below). Similarly, the observed CFC-12 vmr profile can be simulated reasonably well using the entrainment times calculated by *Mote et al.* [1998] or *Minschwaner et al.* [1996], or even allowing for unmixed ascent, provided the ascent rates are further reduced. Figure 3b demonstrates that the observed ethane profile can only be simulated adequately if the 30% slower ascent rates are combined with a much lower chlorine atom concentration because ethane is insensitive to the entrainment time. The observations of CO, however, can only be simulated well

using the standard ascent rate profile. CO is quite insensitive to moderate changes in chlorine as well as to the entrainment time but sensitive to the ascent rates (see figure 3c). This is even more clearly demonstrated in Figure 3d, which shows the 1-D model predictions for the CO/ethane correlation for slowed ascent with lower chlorine concentrations. Similarly, a reasonable fit to the CO/ethane correlation cannot be obtained for any combination of "fast" chemistry and accelerated ascent rates. In summary, the ascent rates derived from the heating rate calculations appear to be in excellent agreement with the observations of the short-lived species and can be constrained by our 1-D model calculations to better than 20%.

Long-lived species. If the chemical loss term in equation (1) is small compared to the quasi-horizontal mixing term, the simulated altitude profiles should be mostly sensitive to the entrainment times and the entrained mid-latitude mixing ratios. The relative influence of chemistry should increase with decreasing lifetime. Figures 4a to 4i show the measured vmr profiles in the tropics for CH_4, CFC-11, CFC-12, CFC-113, CFC-114, CH_3Cl, CH_3Br, H-1211 and H-2402, respectively. Also plotted are the average mid-latitude profiles used as input for the 1-D model (see section 3) and results from our 1-D model simulations. Profiles were computed using the tropical pipe model (with chemical losses only, i.e., no entrainment of mid-latitude air) and for five other entrainment time schemes: altitude independent averages for τ_e of 4 months, 8.5 months, 13.5 months (as calculated by *Volk et al.* [1996]) and two different altitude dependent entrainment time profiles as calculated by *Mote et al.* [1998] and *Minschwaner et al.* [1996]. Both of these studies result in comparably slow mixing over the 16 and 20 km altitude range – slightly slower than the 13.5 month average based on the study by *Volk et al.* (see section 5 for further discussion of these studies compared to our result). We note that not all model results are shown for all species in figure 4.

The tropical pipe model has chemistry as the sole loss term, and thus predicts very small vertical gradients for the longest lived tracers such as CH_4, CFC-12 and CFC-114. Because the altitude profiles of all long-lived species, as expected, exhibit lower vmrs in photochemically

older air at mid–latitudes, stronger mixing (i.e., shorter entrainment times) into the tropical upwelling region causes the concentrations in the tropics to fall off more quickly with altitude. Consequently, the different entrainment time schemes predict stronger altitude gradients as the characteristic mixing time scale decreases.

The data clearly show that the observed concentrations are strongly overestimated when unmixed ascent is assumed. The calculations based on *Mote et al.* and *Minschwaner et al.* also predict considerably smaller altitude gradients than observed.

The best fit to all species simulated is achieved using an altitude independent entrainment time of 8.5 months. Simulations using a 4 month entrainment time scale are shown to demonstrate the sensitivity of the predicted profiles to a 50% reduction in the entrainment time scale. The simulation using $\tau_e = 4$ months clearly underestimates the observed vmr profiles of all species. We would like to emphasize that the entrainment time of 8.5 months provides an excellent overall fit to a set of compounds spanning a range of photochemical lifetimes of 1.5 to 350 years at 420 K. While the simulations for various τ_e of the species that become more influenced by local chemistry (e.g. methyl bromide and the halons), as expected, are less separated than the simulations for the longer-lived species, the 8.5 month entrainment time still can be identified as the best representation of the data because the altitude profiles are more pronounced and the data exhibits less scatter (with the exception of H-2402, which has very low concentrations close to the LOD). Our conclusions are further supported by excellent agreement between model and measurements of tracers that have different chemical loss mechanisms and altitude dependencies of their loss rates, e.g. CH_3Cl (whose lifetime decreases by only a factor of two between 370 and 500K) and CFC-11 (whose lifetime decreases by a factor of 15 between 370 and 500K; see table 1).

It is conceivable that there is vertical structure to the entrainment times; e.g. faster entrainment at lower altitudes that decreases with increasing altitude. However, the scatter in the

data, especially the lower altitude observations, does not allow us to extract information concerning the altitude dependence of τ_e from our 1-D model. For example, if we assume an increasing entrainment time with altitude, e.g. scale the shape of the entrainment time profile of *Mote et al.* [1998] to an average of 8.5 months between 16 and 20.5 km, the predicted profiles are very similar to those shown in figure 4 for $\tau_e = 8.5$ months and provide an equally good fit to the observed tracer profiles.

Uncertainty: It is very difficult to mathematically describe an overall uncertainty in our model results for τ_e. Uncertainties are introduced by variations in the input data, error bars on the kinetic data and empirical relationships applied in the PSS model. Some of these input parameters (e.g. chlorine radicals and ascent rates) can in turn be constrained by our simulations better than their "allowable" uncertainty from independent estimates.

The scatter in our measurements of both tropical and mid-latitude profiles introduces additional uncertainty into the best fit estimate. This scatter is caused in part by limitations of the instrument in the case of the longest-lived species since the observed decrease of the mixing ratios of the CFC, CH_4 and CH_3Cl mixing ratios is only on the order of 5 to 10% over the entire altitude range. This is a small change, which is only about a factor of 5 or so larger than the overall precision of the measurement. Additional scatter may be produced by weak seasonal variations in the tropospheric concentrations (e.g. in the case of CH_4 and CH_3Cl). Another factor is the area in which the flights were performed. The typical seasonal variation in the synoptic conditions in the Pacific south of Hawaii causes a change in the source areas from which air is brought to the region [e.g., *Hess et al.*, 1996]. Both CH_4 and methyl chloride have significant biomass burning sources [*Blake et al.*, 1996b], methyl chloride also has a marine source and CFC are mainly emitted from urban areas. The combination of these effects can cause variations in the boundary conditions (reflected in the scatter at the lowest altitude level) that propagate to higher altitudes in the tropics. However, these factors will only cause systematic errors in our estimate of

τ_e only if any of the different source regions would be more strongly represented during certain sampling times than others. Since the study was carried out over a time of almost two years and since the photochemical ages of the air masses sampled at higher altitudes in the tropics span another two years or so, none of these effects should cause errors that are larger than those represented by the scatter of the observed data.

Since the most sensitive input parameter is the mid-latitude profile, we performed simulations for selected tracers using the upper and lower standard deviation of the mid-latitude profiles as model input. The average results for CH_4, CFC-11, CFC-12 and CFC-113 are 13.0 months for the upper limit of the mid-latitude profiles and 5.5 months for the lower limit. These limits would also encompass more than 90% of the single measurements of all tracers made above 440 K in the tropics. We therefore report an average characteristic entrainment time scale of 8.5^{+5}_{-3} months.

This range for the entrainment time scale also encompasses the values for τ_e found using the various (individual) assumptions regarding the concentration of atomic Cl described above, the ±20% uncertainty for the ascent rate estimated based on the comparison of modeled and measured CO, and the ±25% uncertainty in measured OH. While the uncertainties in most of the rate coefficients of the key loss terms are also encompassed by the 8.5^{+5}_{-3} month range for τ_e, we note that consideration of the *DeMore et al.* [1997] uncertainties for the kinetic processes that limit production and loss of CO would lead to a larger range for τ_e. However, *Herman et al.* [1998b] suggest, based on a detailed analysis of tropical measurements of CO, that the actual uncertainties of the CO production and loss reactions are considerably smaller than the uncertainties given by *DeMore et al.* [1997].

5. Discussion

The sensitivity analysis described above provides reasonable evidence that the uncertainty in the model parameters for ascent rates and the concentration of Cl yields a well

constrained mean entrainment time scale of 8.5^{+5}_{-3} months averaged over the altitude range of 16

to 20.5 km. We have shown that the model ascent rates cannot be slowed down or increased by

more than 20%, because attempts to offset this by changing the chemistry and/or the entrainment

time scale give model results that do not agree with at least some of the measured tracer vmr

profiles. Similarly, a change of the entrainment time scale cannot be offset with slowed or

accelerated chemistry without failing to simulate one or more of the observed tracer profiles,

which gives our retrieved parameters a high level of confidence.

Comparison with other studies. Our result for the average entrainment time scale of 8.5

months agrees well with results from two recently published studies. *Herman et al.* [1998a] used

the same basic model approach to simulate altitude profiles of N_2O and CH_4 measured between

the surface and 32 km altitude by the ALIAS II balloon-borne instrument. They calculated a value

for τ_e of 6 months for altitudes below 20 km, and of 16 months between 20 and 28 km altitude.

An estimate for τ_e of about 5.5 to 7 months can be inferred from observations published in *Tuck*

et al. [1997] (see figure 18 in that review). This result is not based on chemical tracer

observations, but uses a statistical analysis of 880 individual ECMWF back-trajectories to infer

the percentage of air within 10 degrees of the equator originating from mid-latitudes as a function

of potential temperature.

However, our result for τ_e is significantly different from the entrainment times calculated

by *Volk et al.* [1996], *Minschwaner et al.* [1996] and *Mote et al.* [1998]. Their results, as shown in

figure 4, all lead to similar altitude profiles of the long- and medium long-lived tracers that

predict a smaller vertical gradient than the observed profiles. Whether these discrepancies can be

explained by different models, measurements or methods used to derive the entrainment times is·

discussed below.

The study by *Mote et al.* [1998] is based on harmonic analysis of water vapor and CH_4

observations made by the HALOE instrument. The calculated entrainment time is less than 5

months at 16 km and then increases sharply to more than 30 months at 20 km altitude. However, especially below 19 km, where our results are very well constrained by the short-lived tracers, the HALOE data are quite uncertain and the results of *Mote et al.* [1998] are largely based on extrapolation. In the middle stratosphere where HALOE provides very accurate measurements, the mixing times calculated by *Mote et al.* [1998] agree well with those calculated by *Herman et al.* [1998a].

Minschwaner et al. [1996] also calculated a slower entrainment time scale than found here, increasing from 4 to about 18 months for the 16 to 20 km altitude range, respectively, based on an analysis of balloon and aircraft *in situ* measurements of N_2O [*Goldan et al.*, 1980; *Goldan et al.*, 1981; *Vedder et al.*, 1980; *Vedder et al.*, 1978]. *Minschwaner et al.* also calculate entrainment rates based on N_2O data collected on the ER-2 during ASHOE/MAESA and SPADE (lower stratosphere) and from the CLAES instrument on board the UARS satellite (middle stratosphere) which yields faster mixing (τ_e increasing from 7 to 14 months between 380 to 470 K, respectively). However, the Goldan-Vedder N_2O data agree better with the ALIAS II based results for the middle stratosphere. Additional estimates of τ_e are made based on observations of CFC-11. The large scatter, especially in the Goldan-Vedder and CLAES N_2O observations and the large differences between the individual estimates of τ_e based on the various data sets, results in an overall uncertainty of more than 50% below 500K in the entrainment time estimates by *Minschwaner et al.* [1996]. The uncertainty approaches 100% at lower altitudes. Similar to *Mote et al.* [1998], the results of *Minschwaner et al.* probably are more accurate in the middle stratosphere and are largely based on extrapolation in the lower tropical stratosphere.

In contrast, the study by *Volk et al.* [1996] is entirely based on data obtained with the ER-2 at altitudes between 16 and 21 km. A suite of compounds with comparably long atmospheric lifetimes is used, with H-1211 being the shortest lived species analyzed. Individual entrainment times were inferred from the correlations of each tracer either with ozone (NO_y,

CFC-113, CFC-12, N_2O and CH_4) or N_2O (H-1211, methyl chloroform, CCl_4, and CFC-11) which were then averaged to give a value for τ_e of 13.5 months. Although the individual error bars applied to most of the species at the low end of the photochemical lifetimes covered overlap with our result, the uncertainties attributed to entrainment times inferred from the longer lived species do not. Since the photochemistry used in *Volk et al.* is also based on the same PSS model used here, there are only a few slight differences between the lifetimes reported by *Volk et al.* and our calculation (see table 1) that can be explained by different growth rates prior to 1994 compared to 1996/1997 and differences in the radical field calculated by the PSS model. However, there is a significant difference between the altitude profiles that were measured at mid-latitudes by *Volk et al.* and the mid-latitude profile measured by us. This is demonstrated in Figure 5, using CFC-113 as an example. To investigate this further, we simulated the ASHOE/MAESA 1994 data that was used by *Volk et al.* with our 1-D model. Our results do agree very well with those of *Volk et al.*, producing best fit entrainment times of 17 months for N_2O and CFC-12, and 32 months for CFC-113 (see figure 4 in *Volk et al.* [1996]).

There are several possible explanations for the apparent change in τ_e between 1994 and the time period of our study (1995 to 1997) that will be briefly discussed below.

First, the lower stratospheric dynamics during ASHOE/MAESA may have indeed been different than during STRAT/POLARIS. While our study covers a time period of about two years, and therefore averages over a complete period of the QBO, ASHOE/MAESA was carried out between March and November 1994 [*Tuck et al.*, 1997b]. This period marks the end of an easterly phase of the QBO, which may have had an influence on the tracer altitude profiles owing to increased downward transport at mid-latitudes. The mixing ratio of CH_4, for example, can be reduced between 30°S and 45°S by up to 10% between the 100 mbar and 65 mbar pressure levels compared to the two-year average mixing ratios [*W. Randel*, private communication]. Similar reductions in the mixing ratios of the other long lived tracers may be conceivable, potentially

inducing a low bias to the data used by *Volk et al.* compared to the long-term mean profile at mid-latitudes. Our data set, however, did not show significant differences in the mid-latitude profiles of long-lived tracers between the two QBO phases covered.

The different tracer distributions observed in 1994 could also reflect interannual variations in stratospheric dynamical activity independent of the QBO. A second possible explanation arises from perturbations in heating due to enhancements in stratospheric aerosol loading immediately following the eruption of Mt. Pinatubo in June 1991. These perturbations had a large effect on the stratospheric circulation [e.g., *Grant et al.*, 1992; *Kinne et al.*, 1992]. It has recently been suggested that HALOE observations of a ~15% reduction in the mixing ratio of upper stratospheric CH_4 between 1991 and 1997 was due to a longer-term effect of Pinatubo aerosols on stratospheric circulation [*Nedoluha et al.*, 1998]. If this hypothesis is shown to be correct, than it is likely that residual effects of the Pinatubo aerosol may be responsible for the significant differences in the mid-latitude tracer profiles observed between 1994 and 1996/1997 (e.g., figure 5).

Third, while the same latitude bands (30-55°) were used in both studies to define mid-latitudes, the spatial coverages of the two study areas are very different and may also bias the retrieved mid-latitude tracer profiles. A dominant fraction of mid-latitude data used by *Volk et al.* was taken in the southern hemisphere during flight operations out of Christchurch, NZ (44°S, 167°E) between April and October 1994. Especially during the late phase of the experiment, the edge of the Antarctic vortex was observed as far north as 53°S. It is therefore conceivable that the mid-latitude profiles used by *Volk et al.* may include air masses of polar character, thus biasing the average altitude profiles the long-lived species to lower concentrations than what may be characteristic for air that typically mixes into the tropical upwelling region. This is particularly important since the data was filtered only by latitude [*M. Volk*, private communication]. Our mid-latitude profiles, on the other hand, were mainly synthesized from "stair-step" flights based out of

Moffett Field, CA (37°N, 122°W) and the northern fractions of transit flights between Moffett Field and Hawaii that included a dive between 30 and 33°N. A few points exhibiting a tropical signature (as determined by the NO_y/O_3 ratio) were filtered out of our mid-latitude data set.

A fourth possible explanation arises from the fact that one mid-latitude data set is mostly from data acquired in the southern hemisphere (SH) while the other one is exclusively comprised of northern hemispheric (NH) observations. Since there is stronger planetary wave activity in the NH than in the SH, a possible result could be a real asymmetry in the mixing processes of the lower stratosphere. Assuming that the mean profiles were indeed representative of the average mid-latitude concentrations of long-lived tracers in the SH and NH lower stratosphere, our findings would generally be in line with more vigorous mixing between the tropics and mid-latitudes in the NH compared to the SH.

While all the effects described above may have had an influence on the calculated entrainment time scale, it is not possible to clearly distinguish between these effects using the available data.

6. Conclusions and Atmospheric Implications

This study is the first analysis to investigate lower stratospheric dynamics in the tropics using a set of tracers with such a large span of photochemical lifetimes (less than one month to 350 years at 420 K). We have used C_2Cl_4, ethane, CO and the CO *vs.* ethane correlation plot to constrain the parameter set used to simulate the observed altitude profiles of the longer lived species. The tropical profiles of all species examined can be described with a single average entrainment time scale of 8.5^{+5}_{-3} months for the 16 - 20.5 km altitude band, one unique profile of radicals and photolysis rates, and the same two-year mean ascent rate profile. Our transport scheme agrees well with the mean ascent rate provided from an independent radiative heating model, and our chemistry scheme is consistent with *in situ* measurements made on board the ER-2 by the Harvard group [*Wennberg et al.*, 1998].

Our analysis yields an entrainment time scale that is shorter than that reported by earlier studies [*Minschwaner et al.*, 1996; *Mote et al.*, 1998; *Volk et al.*, 1996] but agrees well with two very recently published estimates for τ_e [*Herman et al.*, 1998a; *Tuck et al.*, 1997a]. However, we were able to reproduce calculations resulting in a significantly longer entrainment time using the data that was measured in 1994 and used in the study published by *Volk et al.* [1996]. This result may point towards a large interannual variability in the entrainment times that may be caused by the QBO, by residual effects of the Mt. Pinatubo eruption in 1991, or by an asymmetry between the mixing from the two hemispheres into the tropics.

A shorter entrainment time scale allows for extra-tropical air to more quickly mix into the large-scale tropical ascent region than previously believed. This has a direct impact on assessment models used, for example, to simulate the influence of aircraft emissions (particularly those of a potential HSCT fleet) on the chemistry of the stratosphere. An indication of a possible asymmetry between entrainment times characteristic for the northern and southern hemisphere with faster mixing from the north would also impact HSCT assessment calculations, since most of the

emissions would be expected in the northern mid-latitudes. Faster transport of mid-latitude air into the tropics also impacts the globally averaged lifetimes of longer-lived halogenated species, NO_y, N_2O, CH_4, etc., which directly influences assessments of stratospheric ozone depletion and global warming potentials.

Our results further suggest an important contribution of short-lived chlorine containing species to the Cl_y budget as has been suggested by [e.g., *Ko et al.*, 1997; *Schauffler et al.*, 1998b; *Solomon et al.*, 1994]. These compounds seem to be poorly represented by empirical relationships to estimate Cl_y from longer-lived tracer concentrations [e.g., *Woodbridge et al.*, 1995] that are presently used in many models of lower tropical stratospheric chemistry.

Table 1: Simulated tracers: average lifetimes, main loss reactions, interhemispheric gradients,

average growth rates for the 1994-1997 period and boundary conditions for the 1-D model.

Species	Boundary conc. [pptv]	Average lifetime (at theta level) [years]				Main loss process	Inter-hemispheric gradient*	Growth rate [s-1]
		370 K	420 K	470 K	500 K			
CO	$5.8 \cdot 10^4$	0.26	0.26	0.27	0.27	OH	1	0
C_2Cl_4	0.40	0.33	0.06	0.05	0.05	OH, Cl	1.40	0
C_2H_6	400	0.69	0.11	0.07	0.05	OH, Cl	1.23	0
H-2402 (CF_2BrCF_2Br)	0.44	5.40	1.41	0.74	0.45	hv	1.08	1.22E-09
H-1211 (CF_2ClBr)	3.42	7.00	1.66	0.86	0.52	hv	1.04	1.10E-09
CH_3Br	9.50	7.43	2.26	1.19	0.75	OH	1.10	0
CH_3Cl	576˙	13.3	11.4	7.38	6.24	OH	1	0
CFC-11 ($CFCl_3$)	267	26.1	5.60	2.80	1.70	hv	1.01	-8.7E-11
CH_4	$1.715 \cdot 10^6$	145	114	62.0	50.1	OH, Cl	1.01	5.5E-11
CFC-113 (CF_3CCl_3)	83	149	32.1	15.9	9.63	hv	1.01	4.79E-11
CFC-12 (CF_2Cl_2)	539	331	69.8	32.8	19.65	hv	1.01	4.21E-10
CFC-114 (CF_2ClCCl_3)	14.0	1588	356	161	100	hv	1	0

* Correction factor for the measured northern hemispheric average profiles between 370 and 420 K

31

Figure captions

Figure 1: Chlorine atom concentration profiles versus potential temperature for the lower tropical troposphere. Compared are three PSS model results for different input parameter sets and the optimum chlorine atom concentration profile retrieved to match the short-lived tracer observations. See text for details.

Figure 2: Mixing ratios of CO (a), ethane (b), and tetrachloroethene (c) in the tropical lower stratosphere versus potential temperature. Plotted are the individual measurements (black dots) and 1-D model results using three different chlorine radical altitude profiles. Profiles were calculated by the PSS model using the standard input data set based on the WAS measurements (gray dashed line) and the upper limit chlorine concentration from the PSS model (gray dotted line). The black solid line shows the chlorine radical profile that was chosen to best fit the measured short-lived tracers; (d) correlation plot of CO versus ethane. The model results are shown as in Figure 2a-c. The higher resolution ALIAS data (3-sec) was averaged over the WAS can sampling intervals to allow the direct comparison.

Figure 3: CFC-12 (a) mixing ratios (black dots) versus potential temperature in the tropics. Shown are 1-D model results for 8.5 months entrainment time with unaltered ascent rates (reference case; gray solid line) and for a 13.5 months entrainment time [*Volk et al.*, 1996] using ascent rates that were 30% slowed (black solid line). Also shown is a result for the tropical pipe model with 30% slower ascent rates for comparison (gray dotted line). Ethane (b) and CO (c) mixing ratios in the tropics versus potential temperature (black dots). Also plotted are the reference case (gray solid line) and the 1-D model results for 30% slowed ascent rates and 13.5 months entrainment time with unaltered chemistry (black solid line) and lower chlorine atom

concentrations (gray dashed line); (d) as in figure 3b and c, but for the CO/Ethane correlation.

Figure 4: Long-lived tracer mixing ratios as measured in the tropical lower stratosphere versus potential temperature (θ). Plotted are the individual samples (black dots) and the 1-D model results for tropical pipe (black solid line), entrainment times as calculated by *Mote et al.* [1998] (orange dotted line), *Minschwaner et al.* [1996] (gray dashed line), *Volk et al.* [1996] (green solid line), and entrainment times of 8.5 months (red solid line) and 4 months (blue dashed line). Also shown are the measured mid-latitude profiles of the respective tracer (magenta solid line). The data are averages over 5° potential temperature intervals, the vertical error bars show the ranges of θ, the horizontal error bars are 1σ standard deviations of the measurements. Tracers shown are (a) CH_4, (b) CFC-12, (c) CFC-11, (d) CFC-113, (e) CFC-114, (f) CH_3Cl, (g) CH_3Br, (h) H-1211 and (i) H-2402. Note that not all model results are shown for all species.

Figure 5: Comparison of the mid-latitude CFC-113 concentration profile versus potential temperature (θ) as measured by *Volk et al.* [1996] (gray line, no standard deviations available) and in this study (black line). Error bars are θ range in the vertical and 1σ standard deviations in the horizontal.

References

Atlas, E., F. Flocke, S. Schauffler, D.R. Blake, and F.S. Rowland, Observations of marine alkyl nitrate emissions in the Pacific during PEM-Topics, *J. Geophys. Res., in prep*, 1998.

Avallone, L.M., and M.J. Prather, Photochemical evolution of ozone in the lower tropical stratosphere, *J. Geophys. Res., 101*, 1457-1461, 1996.

Blake, D.R., N.J. Blake, T.W. Smith, O.W. Wingenter, and F.S. Rowland, Nonmethane hydrocarbon and halocarbon distributions during ASTEX/MAGE, June 1992, *J. Geophys. Res., 101*, 4501-4510, 1996a.

Blake, N.J., D.R. Blake, B.C. Sive, T.Y. Chen, and F.S. Rowland, Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region, *J. Geophys. Res.*, 24151-24164, 1996b.

Boering, K.A., B.C.D. Jr., S.C. Wofsy, M. Loewenstein, J.R. Podolske, and E.R. Keim, Tracer-tracer-relationships and lower stratospheric dynamics: CO_2 and N_2O correlations during SPADE, *Geophys. Res. Lett., 21*, 2567-2570, 1994.

Boering, K.A., S.C. Wofsy, B.C. Daube, H.R. Schneider, M. Loewenstein, J.R. Podolske, and T.J. Conway, Stratospheric mean ages and transport rates from observations of carbon dioxide and nitrous oxide, *Science, 274*, 1340-1343, 1996.

Daniel, J.S., S.M. Schauffler, W.H. Pollock, S. Solomon, A. Weaver, L.E. Heidt, R.R. Garcia, E.L. Atlas, and J.F. Vedder, On the age of stratospheric air and inorganic chlorine and bromine release, *J. Geophys. Res., 101* (D11), 16757-16770, 1996.

DeMore, W.B., S.P. Sander, C.J. Howard, A.R. Ravishankara, D.M. Golden, C.E. Kolb, R.F. Hampsen, M.J. Kurylo, and M.J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation No. 12, Jet Propulsion Laboratory, Pasadena, CA, 1997.

Dlugokencky, E.J., K.A. Masarie, P.P. Tans, T.J. Conway, and X. Xiong, Is the amplitude of the methane seasonal cycle changing?, *Atmos. Environ.*, *31*, 21-26, 1997.

Elkins, J.W., D.W. Fahey, J.M. Gilligan, G.S. Dutton, T.J. Baring, C.M. Volk, R.E. Dunn, R.C. Myers, S.A. Montzka, P.R. Wamsley, A.H. Hayden, J.H. Butler, T.M. Thompson, T.H. Swanson, E.J. Dlugokencky, P.C. Novelli, D.F. Hurst, J.M. Lobert, S.J. Ciciora, R.J. McLaughlin, T.L. Thompson, R.H. Winkler, P.J. Fraser, L.P. Steele, and M.P. Lucarelli, Airborne gas chromatograph for in-situ measurements of long-lived species in the upper troposphere and lower stratosphere, *Geophys. Res. Lett.*, *23* (4), 347-350, 1996.

Fahey, D.W., C.S. Eubank, G. Hübler, and F.C. Fehsenfeld, Evaluation of a Catalytic Reduction Technique for the Measurement of Total Reactive Odd-Nitrogen NOy in the Atmosphere, *J. Atmos. Chem.*, *3*, 435-468, 1985.

Flocke, F., E. Atlas, S. Madronich, S. S.M., K. Aikin, J.J. Margitan, and T.P. Bui, Observations of methyl nitrate in the lower stratosphere during STRAT: Implications for its gas phase production mechanisms, *Geophys. Res. Lett.*, *25*, 1891-1894, 1998.

Frazer, P.J., D.E. Oram, C.E. Reeves, S.A. Penkett, and A. McCulloch, Sothern hemispheric halon trends (1978-1998) and global halon emissions, *J. Geophys. Res.*, *in press*, 1998.

Gao, R.S., D.W. Fahey, L.A. DelNegro, S.G. Donelly, E.R. Keim, L. Teverovski, P.O. Wennberg, T.F. Hanisco, M.H. Proffitt, J.J. Margitan, J.C. Wilson, J.W. Elkins, R.M. Stimpfle, R.C. Cohen, C.T. McElroy, T.P. Bui, R.J. Salawitch, S.S. Brown, A.R. Ravishankara, R.W. Portmann, M.K.W. Ko, D.K. Weisenstein, and P. A. Newman, A comparison of observations and model simulations of NO_x/NO_y in the lower stratosphere, *Geophys. Res. Lett.*, *submitted*, 1998.

Goldan, P.D., W.C. Kuster, D.L. Albritton, and A.L. Schmeltekopf, Stratospheric $CFCl_3$, CF_2Cl_2, and N_2O height profile measurements at several latitudes, *J. Geophys. Res.*, *85*, 413-423, 1980.

Goldan, P.D., W.C. Kuster, A.L. Schmeltekopf, and F.C. Fehsenfeld, Correction of atmospheric

N_2O mixing ratio data, *J. Geophys. Res.*, *86*, 5385-5386, 1981.

Grant, W.B., J. Fishman, E.V. Browell, V.G. Brackett, D. Nganga, A. Minga, B. Cros, R.E. Veiga, C.F. Butler, M.A. Fenn, and G.D. Nowicki, Observations of reduced ozone concentrations in the tropical stratosphere after the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, *19*, 1109-1112, 1992.

Hall, T.M., and D.W. Waugh, Tracer transport in the tropical stratosphere due to vertical diffusion and horizontal mixing, *Geophys. Res. Lett.*, *24*, 1383-1386, 1997.

Heidt, L.E., J.F. Vedder, W.H. Pollock, and R.A. Lueb, Trace gases in the antarctic atmosphere, *J. Geophys. Res.*, *94*, 11599-11611, 1989.

Herman, R.L., D.C. Scott, C.R. Webster, R.D. May, E.J. Moyer, R.J. Salawitch, Y.L. Yung, G.C. Toon, B. Sen, J.J. Margitan, K.H. Rosenlof, H.A. Michelsen, and J.W. Elkins, Tropical entrainment time scales inferred from stratospheric N2O and CH4 observations, *Geophys. Res. Lett.*, *25*, 2781-2784, 1998a.

Herman, R.L., C.R. Webster, R.D. May, D.C. Scott, E.J. Moyer, P.O. Wennberg, T.F. Hanisco, E.J. Lanzendorf, R.J. Salawitch, Y.L. Yung, J.J. Margitan, and T.P. Bui, Measurements of CO in the upper troposphere and lower stratosphere, *Chemosphere, in press*, 1998b.

Hess, P.G., N. Srimani, and S.J. Flocke, Trajectories and related variations in the chemical composition of air for the Mauna Loa Observatory during 1991 and 1992, *J. Geophys. Res.*, *99* (D9), 14543-14568, 1996.

Hoell, J., Pacific Exploratory Mission in the Tropics; September 1996, *J. Geophys. Res.*, *submitted*, 1998.

Holton, J.R., P.H. Haynes, M.E. McIntyre, A.R. Douglass, R.B. Rood, and L. Pfister, Stratosphere-Troposphere Exchange, *Rev. Geophys.*, *33*, 403-439, 1995.

Jeagle, L., D.J. Jacob, P.O. Wennberg, C.M. Spivakovski, T.F. Hanisco, E.J. Lanzendorf, E.J. Hintsa, D.W. Fahey, E.R. Keim, M.H. Profitt, E. Atlas, F. Flocke, S.M. Schauffler, C.T. McElroy, C. Midwinter, L. Pfister, and J.C. Wilson, Observed OH and HO_2 in the upper

troposphere suggest a major source from convective injection of peroxides, *Geophys. Res. Lett.*, *24* (24), 3181-3184, 1997.

Kinne, S., O.B. Toon, and M. J. Prather, Buffering of stratospheric circulation by changing amounts of tropical ozone: a Pinatubo case study, *Geophys. Res. Lett.*, *19*, 1927-1930, 1992.

Ko, M.K.W., N.D. Sze, C.J. Scott, and D.K. Weisenstein, On the relation between stratospheric chlorine/bromine loading and short-lived tropospheric trace gases, *J. Geophys. Res.*, *102*, 25507-25517, 1997.

May, R.D., and C.R. Webster, Data processing and calibration for tunable diode laser harmonic absorption spectrometers, *J. Quant. Spectrosc. Radiat. Transfer*, *49*, 335-347, 1993.

Michelsen, H.A., G.L. Manney, M.R. Gunson, C.P. Rinsland, and R. Zander, Correlations of stratospheric abundances of CH_4 and N_2O derived from ATMOS measurements, *Geophys. Res. Lett.*, *25*, 2777-2780, 1998.

Michelsen, H.A., R.J. Salawitch, M.R. Gunson, C. Aellig, N. Kaempfer, M.M. Abbas, M.C. Abrams, T.L. Brown, A.Y. Chang, A. Goldman, F.W. Irion, M.J. Newchurch, C.P. Rinsland, G.P. Stiller, and R. Zander, Stratospheric chlorine partitioning: Constraints from shuttle-borne measurements of [HCl], [$ClNO_3$], and [ClO], *Geophys. Res. Lett.*, *23*, 2361-2364, 1996.

Minschwaner, K., A.E. Dessler, J.W. Elkins, C.M. Volk, D.W. Fahey, M. Loewenstein, J.R. Podolske, A.E. Roche, and K.R. Chan, Bulk properties of isentropic mixing into the tropics in the lower stratosphere, *J. Geophys. Res.*, *101*, 9433-9439, 1996.

Minschwaner, K., R.J. Salawitch, and M.B. McElroy, Absorption of solar radiation by O_2: Implications for O_3 and lifetimes of N_2O, $CFCl_3$ and CF_2Cl_2., *J. Geophys. Res.*, *98*, 10543-10561, 1993.

Montzka, S.A., J.H. Butler, R.C. Myers, T.M. Thompson, T.H. Swanson, A.D. Clarke, L.T. Lock, and J.W. Elkins, Decline in the tropospheric abundance of halogen from halocarbons:

Implications for stratospheric ozone depletion, *Science, 272*, 1318-1322, 1996.

Mote, P.W., T.J. Dunkerton, M.E. McIntyre, E.A. Ray, P.H. Haynes, and J.M. Russell III, Vertical velocity, vertical diffusion, and dilution by midlatitude air in the tropical lower stratosphere, *J. Geophys. Res., 103*, 8651-8666, 1998.

Mote, P.W., K.H. Rosenlof, M.E. McIntyre, E.S. Carr, J.C. Gille, J.R. Holton, J.S. Kinnersley, H.C. Pumphrey, J.M. Russell III, and J.W. Waters, An atmospheric tape recorder: The imprint of tropical tropopause temperatures on stratospheric water vapor, *J. Geophys. Res., 101*, 3989-4006, 1996.

Murphy, D.M., D.W. Fahey, M.H. Proffitt, S.C. Liu, K.R. Chan, C.S. Eubank, S.R. Kawa, and K.K. Kelly, Reaetive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res., 98*, 8571-8573, 1993.

Nedoluha, G.E., D.E. Siskind, J.T. Bacmeister, R.M. Bevilacqua, and J.M.R. III, Changes in upper stratospheric CH_4 and NO_2 as measured by HALOE and implications for changes in transport, *Geophys. Res. Lett., 25* (987-990), 1998.

Osterman, G.B., B. Sen, G.C. Toon, R.J. Salawitch, J.J. Margitan, J.-F. Blavier, D.W. Fahey, and R.S. Gao, The partitioning of reactive nitrogen species in the summer Arctic stratosphere, *Geophys. Res. Lett., submitted*, 1998.

Plumb, R.A., A "tropical pipe" model of stratospheric transport, *J. Geophys. Res., 101*, 3957-3972, 1996.

Proffitt, M.H., and R.J. McLaughlin, Fast-response dual-beam UV-absorption ozone photometer suitable for use on stratospheric balloons, *Rev. Sci. Instrum., 54*, 1719-1728, 1983.

Randel, W.J., J.C. Gille, A.E. Roche, J.B. Kumer, J.L. Mergenthaler, J.W. Waters, E.F. Fishbein, and W.A. Lahoz, Stratospheric transport from the tropics to mid-latitudes by planetary-wave mixing, *Nature, 365*, 533-535, 1993.

Randel, W.J., F. Wu, J.M. Russell III, and A. Roche, Seasonal cycles and interannual variability in stratospheric CH_4 and H_2O observed in UARS Haloe data, *J.Atmos.Sci, 55*, 163-185,

1998.

Roeth, E.P., R. Ruhnke, G. Moortgat, R. Meller, and W. Schneider, UV-VIS absorption cross sections and quantum yields for use in photochemistry and atmospheric modeling. Part 2: organic substances, Forschungszentrum Juelich, Juelich, 1998.

Rosenlof, K.H., Seasonal cycle of the residual mean meridional circulation in the stratosphere, *J. Geophys. Res.*, *100*, 5173-5191, 1995.

Salawitch, R.J., S.C. Wofsy, P.O. Wennberg, R.C. Cohen, J.G. Anderson, D.W. Fahey, R.S. Gao, E.R. Keim, E.L. Woodbridge, R.M. Stimpfle, P. Koplow, D.W. Kohn, C.R. Webster, R.D. May, L. Pfister, E.W. Gottlieb, H.A. Michelsen, G.K. Yue, M.J. Prather, J.C. Wilson, C.A. Brock, H.H. Jonsson, J.E. Dye, D. Baumgardner, M.H. Proffitt, M. Loewenstein, J.R. Podolske, J.W. Elkins, G.S. Dutton, E.J. Hintsa, A.E. Dessler, E.M. Weinstock, K.K. Kelly, K.A. Boering, B.C. Daube, K.R. Chan, and S.W. Bowen, The diurnal variation of hydrogen, nitrogen, and chlorine radicals: implications for the heterogeneous production of HNO2, *Geophys. Res. Lett.*, *21*, 2551-2554, 1994.

Schauffler, S.M., E. Atlas, F. Flocke, R.A. Lueb, V. Stroud, and W. Travnicek, Measurements of bromine-containing organic compounds at the tropical tropopause, *Geophys. Res. Lett.*, *25* (3), 317-320, 1998a.

Schauffler, S.M., E.L. Atlas, D.R. Blake, F. Flocke, X.X. Tie, R.A. Lueb, J.M. Lee-Taylor, V. Stroud, and W. Travnicek, Distributions of brominated organic compounds in the troposphere and lower stratosphere, *J. Geophys. Res.*, *submitted*, 1998b.

Schoeberl, M.R., A.E. Roche, J.M. Russell III, D. Ortland, P.B. Hays, and J.W. Waters, An estimation of the dynamical isolation of the tropical lower stratosphere using UARS wind and trace gas observations of the quasi-biennial oscillation, *Geophys. Res. Lett.*, *24* (53-56), 1997.

Scott, S.G., T.P. Bui, K.R. Chan, and S.W. Bowen, The Meteorological Measurement System on the NASA ER-2 aircraft, *J. Atmos. and Oceanic Technol.*, *7*, 525-540, 1990.

Sen, B., G. B. Osterman, R. J. Salawitch, G. C. Toon, J. J. Margitan,, J.-F. Blavier, A.Y. Chang, R.D. May, C.R. Webster, R.M. Stimpfle, G.P. Bonne, P.B. Voss, K.K. Perkins, J.G. Anderson, R.C. Cohen, L.C. Koch, J.W. Elkins, G.S. Dutton, P.A. Romashkin, E.L. Atlas, S.M. Schauffler, and M. Loewenstein, The budget and partitioning of stratospheric chlorine during Photochemistry of Ozone Loss in the Arctic Region in Summer, *J. Geophys. Res., this issue*, 1998.

Singh, H.B., M. Kanakidou, P.J. Crutzen, and D.J. Jacob, High concentration and photochemical fate of oxygenated hdrocarbons in the global troposphere, *Nature, 378*, 50-53, 1995.

Solomon, S., R.R. Garcia, and A.R. Ravishankara, On the role of iodine in ozone depletion, *J. Geophys. Res., 99*, 20491-20499, 1994.

Stolarski, R., *1995 Scientific Assessment of the Atmospheric Effects of Stratospheric Aircraft*, National Aeronautics and Space Administration, Washington, D.C., 1995.

Travnicek, W., E.L. Atlas, F. Flocke, and S.M. Schauffler, Measurements of light halogenated tracers during POLARIS and comparison with a long-term record derived from archived tropospheric air samples, in *presented at the 1998 Conference on the Atmospheric Effects of Aviation*, Virginia Beach, VA, April 25 - May1, 1998.

Trepte, C.R., and M.H. Hitchman, Tropical stratospheric circulation deduced from satellite aerosol data, *Nature, 355*, 626-628, 1992.

Tuck, A.F., D. Baumgardner, K.R. Vhan, J.D. Dye, J.W. Elkins, H. S.J., K.K. Kelly, M. Loewenstein, J.J. Margitan, R.D. May, J.R. Podolske, M.H. Proffitt, K.H. Rosenlof, W.L. Smith, C.R. Webster, and J.C. Wilson, The Brewer-Dobson circulation in the light of high altitude *in situ* aircraft observations, *Quart. J. Royal. Meteorol. Soc., 123*, 1-69, 1997a.

Tuck, A.F., W.H. Brune, and R.S. Hipskind, Airborne Southern Hemisphere Ozone Experiment / Measurements for Assessing the Effects of Startospheric Aircraft (ASHOE/MEASA): A road map, *J. Geophys. Res., 102*, 3901-3904, 1997b.

Vedder, J.F., E.C.Y. Inn, B.J. Tyson, and C.A. Boitnott, Measurements of CF_2Cl_2, $CFCl_3$, and N_2O profiles in the lower stratosphere between 2S and 73N latitude, *J. Geophys. Res.*, *86*, 7363-7368, 1980.

Vedder, J.F., B.J. Tyson, R.B. Brewer, C.A. Boitnott, and E.C.Y. Inn, Lower stratosphere measurements of variation with latitude of CF_2Cl_2, $CFCl_3$, CCl_4, and N_2O profiles in the northern hemisphere, *Geophys. Res. Lett.*, *5*, 33-36, 1978.

Volk, C.M., J.W. Elkins, D.W. Fahey, R.J. Salawitch, G.S. Dutton, J.M. Gilligan, M.H. Proffitt, M. Loewenstein, J.R. Podolske, K. Minschwaner, J.J. Margitan, and K.R. Chan, Quantifying transport between the tropical and mid-latitude lower stratosphere, *Science*, *272*, 1763-1768, 1996.

Webster, C.R., R.D. May, C.A. Trimble, R.G. Chave, and J. Kendall, Aircraft (ER-2) laser infrared absorption spectrometer (ALIAS) for *in situ* stratospheric measurements of HCl, N2O, CH4, NO2 and HNO3, *Appl. Opt.*, 454-472, 1994.

Wennberg, P.O., R.C. Cohen, N.L. Hazen, L.B. Lapson, N.T. Allen, T.F. Hanisco, J.F. Oliver, N.W. Lanham, J.N. Demusz, and J.G. Anderson, Aircraft-borne, laser-induced fluorescence instrument for the *in situ* detection of hydroxyl and hydroperoxyl radicals, *Rev. Sci. Instrum.*, *65*, 1858-1876, 1994a.

Wennberg, P.O., R.C. Cohen, R.M. Stimpfle, J.P. Koplow, J.G. Anderson, R.J. Salawitch, D.W. Fahey, E.L. Woodbridge, E.R. Keim, R. Gao, C.R. Webster, R.D. May, D.W. Toohey, L.M. Avallone, M.H. Proffitt, M. Loewenstein, J.R. Podolske, K.R. Chan, and S.C. Wofsy, Removal of stratospheric ozone by radicals: in situ measurements of OH, HO_2, NO, NO_2, ClO, and BrO, *Science, 266*, 398-404, 1994b.

Wennberg, P.O., T.F. Hanisco, L. Jaegle, D.J. Jacob, E.J. Hintsa, E.J. Lanzendorf, J.G. Anderson, R.-S. Gao, E.R. Keim, S.G. Donnelly, L.A. DelNegro, D.W. Fahey, S.A. McKeen, R.J. Salawitch, C.R. Webster, R.D. May, R.L. Herman, M.H. Profitt, J.J. Margitan, E. Atlas, F. Flocke, S.M. Schauffler, C.T. McElroy, J.C. Wilson, C.A. Brock, and T.P. Bui,

Hydrogen radicals, nitrogen radicals, and the production of ozone in the middle and upper troposphere, *Science*, *279*, 49-53, 1998.

Wofsy, S.C., K.A. Boering, B.C. Daube, and M.B. McElroy, Vertical transport rates in the stratosphere in 1993 from observations of CO_2, N_2O and CH_4, *Geophys. Res. Lett.*, *21*, 2571-2574, 1994.

Woodbridge, E.L.et al., Estimates of total organic and inorganic chlorine in the lower stratosphere from in-situ and flask measurements during AASE II, *J. Geophys. Res.*, *100*, 3057-3064, 1995.

ACATS based PSS std
WAS based PSS std.
optimized Cl profile
high chlorine case

(a) (b) (c) (d)